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(54) Catalysts for the (co)polymerization of ethylene

Katalysatoren für die (Co)Polymerisation von Ethylen

Catalyseurs utilisables pour la (co)polymérisation de l'éthylène

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Description

The present invention relates to catalysts for the polymerization of ethylene and its mixtures with olefins $\text{CH}_2=\text{CHR}^{\text{VIII}}$, wherein R^{VIII} is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms, comprising the reaction

5 product of a solid catalyst component containing Ti, Mg and halogen, an alkyl-Al compound and a particular electron donor compound. The catalyst of the invention is suitably used in (co)polymerization processes of ethylene to prepare (co)polymers having narrow Molecular Weight Distribution (MWD). The MWD is an important characteristic of ethylene polymers in that it affects both the rheological behaviour, and therefore the processability, and the final mechanical 10 properties. In particular, in the case of LLDPE, polymers with narrow MWD are suitable for films and injection molding in that deformation and shrinkage problems in the manufactured article are minimized.

The width of the molecular weight distribution for the ethylene polymers is generally expressed as melt flow ratio F/E, which is the ratio between the melt index measured by a load of 21.6 Kg (melt index F) and that measured with a load of 2.16 Kg (melt index E). The measurements of melt index are carried out according to ASTM D-1238 and at 190 °C.

15 A catalyst for preparing ethylene (co)polymers having narrow MWD is described in the European patent application EP-A-373999: the catalyst comprises a solid catalyst component consisting of a titanium compound supported on magnesium chloride, an alkyl-Al compound and an electron donor compound (external donor) selected from monoethers of the formula $\text{R}'\text{OR}^{\text{a}}$. Good results in terms of narrow MWD are only obtained when the solid component also contains an internal electron donor compound (diisobutylphthalate).

20 "EP 449302 discloses catalysts for preparing hyperpure propylene polymers based on a solid catalyst component consisting of a titanium compound and a diether as an internal donor supported on a magnesium dihalide. Similarly EP 546573 describes a process for the production of polyolefins based on the use of a catalyst containing a titanium compound and an internal electron donor compound supported on magnesium chloride. The yield of these polymerization processes, however, is rather low."

25 Catalysts for the polymerization of ethylene and mixtures thereof with one or more olefins $\text{CH}_2=\text{CHR}^{\text{VIII}}$ have been now found, which comprise particular external electron donor compounds and are particularly suitable for the preparation of ethylene (co)polymers with narrow MWD. Furthermore, when the catalysts of the invention are used for the preparation of LLDPE, the products obtained are characterized by a low content of xylene soluble fractions, a property which makes them particularly interesting for applications such as films and materials for the foodstuffs sector. Moreover, the polymers obtained with the catalyst of the invention show interesting rheological properties in that the intrinsic viscosity of the soluble fractions has relatively high values, thus improving the processability of the polymers. In particular, remarkable improvements are found in the processes for preparing very low density ethylene copolymers (VLDPE and ULDPE) wherein the reactor fouling phenomena are significantly reduced.

30 The catalysts of the invention comprise the reaction product of:

35 (a) a solid catalyst component comprising a magnesium halide in the active form as specified and a titanium compound containing at least one Ti-halogen bond;
 (b) an alkyl-Al compound;
 (c) an external electron donor compound selected from diethers, said compounds being reactive with MgCl_2 but not with triethyl-Al under standard conditions.

40 Preferably the electron donor compound (c) is a 1,3-diether.

The reactivity test of compound (c) with respect to triethyl-aluminium is carried out using a potentiometer METRO-HM mod. E 536, equipped with titration table E 535, an automatic burette E 552, a magnetic stirrer E 549 and a titration 45 cell EA 880. A combined electrode EA 281 (Pt/Ag/AgCl/KCl 3M) is used. As titrating agent a 0.5 M AlEt_3 hexane solution is used, which is added to a 0.5 molar benzene solution of the compound to be tested, operating at room temperature and under nitrogen atmosphere. The compound (c) does not show an appreciable variation or jump of potential at the titration equivalence point. The reactivity test of the electron donor compound (c) with MgCl_2 is carried out under the 50 following conditions: into a 100 cm³ glass reactor equipped with mechanical stirrer, 70 cm³ of n-heptane, 12 mmols of anhydrous MgCl_2 activated as hereinbelow described, 2 mmols of electron donor compound (c) are introduced. The mixture is heated at 60 °C for 4 hours (stirring speed 100 r.p.m.), then is filtered off and washed at room temperature with 100 cm³ of n-heptane and dried. The amount of the compound (c) complexed is determined by treatment of the 55 solid with 100 cm³ of ethyl alcohol and gaschromatographic analysis of the solution. The magnesium chloride used in the standard test is prepared as follows: into a 1 litre vibrating mill (Siebtechnik's Vibratom) containing 1.8 Kg of 16 mm diameter stell balls, 50 g of anhydrous MgCl_2 and 6.8 cm³ of 1,2-dichloroethane are introduced under a nitrogen atmosphere. The mixture is milled at room temperature for 96 hours and the solid obtained is dried at 50 °C for 16 hours under vacuum.

The magnesium halide present in the solid component (a) is preferably magnesium chloride in the active form.

The active form of magnesium chloride used in the preparation of solid catalyst components for the polymerization of olefins is well-known in the art. It was first described in USP 4,495,338 and USP 4,476,289 as being characterized by X-ray spectrum wherein the most intense diffraction line appearing in the spectrum of the non active chloride is diminished in intensity and in said spectrum a halo appears, the maximum intensity of which is shifted towards lower angles in comparison to that of the most intense line.

5 Among the titanium compounds containing at least one Ti-halogen bond, those having the formula $Ti(OR^{IX})_{n-y}X_y$, wherein OR^{IX} is a hydrocarbyl radical having 1-12 carbon atoms or a COR^{IX} group X is halogen, n is the titanium valence and y is a number comprised between 1 and n, are preferred.

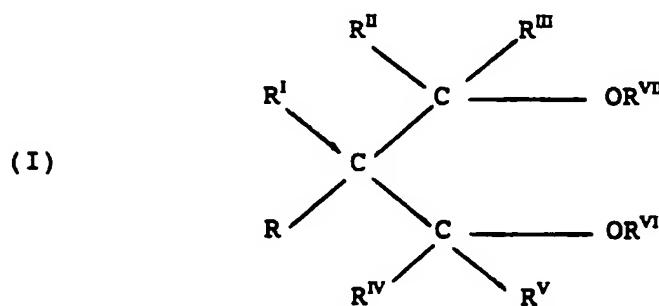
10 The solid component (a) can be suitably prepared by reaction between a titanium compound of the formula $Ti(OR^{IX})_{n-m}X_m$, wherein n is the valence of titanium and m is a number comprised between 0 and n, and a magnesium chloride obtained by dealcoholation of an adduct $MgCl_2.pRX^{OH}$, wherein p is a number from 1 to 6 and RX is a hydro-

carbyl radical having 1-12 carbon atoms. Optionally the reaction can be carried out in the presence of a halogenating compound or a reducing compound or a mixture of the two, or a compound having both halogenating and reducing activity.

15 Examples of preparation of the solid catalyst component are described in USP 4,218,339 and USP 4,472,520. Solid components of the catalyst can also be prepared according to the methods described in USP 4,748,221 and USP 4,803,251. Particulary preferred are the catalyst components endowed with regular morphology, for example spherical or spheroidal. Examples of said components are described in USP 4,399,054 and in Datent aDDlications EP-A-395083. EP-A-553805, EP-A-553806. EP-A-601525 and EP-A-604846.

20 The alkyl aluminium compound (b) is preferably selected from aluminium trialkyls, such as trimethyl-Al, triethyl-Al, triisobutyl-Al, tri-n-butyl-Al, tri-n-octyl-Al. Mixture of Altrialkyls with Al-alkylhalides or Al-alkylsesquihalides such as $AlMe_2Cl$, $AlEt_2Cl$ and $Al_2Et_3Cl_3$ can be used as well as compounds containing two or more Al atoms linked together by O, N atoms or SO_3 or SO_4 groups.

25 The electron donor compound (c) is preferably selected from 1,3-diethers of the formula (I)



40 wherein R, R^1 , R^2 , R^3 , R^4 , R^5 , same or different from each other, are hydrogen or linear or branched alkyl radicals, cycloalkyl, aryl, alkylaryl or arylalkyl radicals having 1-18 carbon atoms, with the provision that R and R^1 cannot both be hydrogen; R^6 and R^7 , same or different from each other, are linear or branched alkyl radicals, cycloalkyl, aryl, alkylaryl or arylalkyl radicals having 1-18 carbon atoms; when radicals from R^1 to R^5 are hydrogen and R^6 and R^7 are methyl, R cannot be methyl; at least two of the radicals from R to R^7 can be linked together to form one or more cyclic structures. These compounds can be advantageously prepared according to what is described in patent EP-361493. Preferably, R^6 and R^7 are methyl and R and R^1 , same or different from each other, are selected from the group consisting of propyl, isopropyl, isobutyl, t-butyl, pentyl, isopentyl, cyclopentyl, hexyl, 1,5-dimethylhexyl, cyclohexyl, methylcyclohexyl, ethylcyclohexyl, heptyl, 3,7-dimethyloctyl, phenyl.

45 Some examples of 1,3-diethers useable in the catalysts of the invention are: 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-diphenyl-1,3-dimethoxypropane, 2,2-dibenzyl-1,3-dimethoxypropane, 2,2-bis-(cyclohexylmethyl)-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dibutoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2-isopentyl-2-isopropyl-1,3-dimethoxypropane, 2,2,4-trimethyl-1,3-dimethoxypentane, 1,1-bis-(methoxymethyl)cyclohexane, (+/-) 2,2-bis-(methoxymethyl)norbornane, 2-isopropyl-2-(3,7-dimethyloctyl)-1,3-dimethoxypropane, 2,2-diisopropyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropane, 2,2-diisopentyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2-heptyl-2-pentyl-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane, 2-isopropyl-2-isobutyl-1,3-dimethoxypropane.

55 The catalysts of the invention are suitably used in processes for the polymerization of ethylene and its mixtures

with olefins $\text{CH}_2=\text{CHR}^{\text{VIII}}$, wherein R^{VIII} is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms, in particular 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, and 1-octene either in liquid or gas phase, thus obtaining polymers characterized by a narrow MWD. For example, high density polyethylene (HDPE; density higher than 0.940) among which ethylene homopolymers and copolymers of ethylene with alpha-olefins having from 3 to 12 carbon atoms; 5 linear low density polyethylene (LLDPE; density lower than 0.940) and linear very low and ultra low density polyethylene (VLDPE and ULDPE; density lower than 0.920, up to 0.880) consisting of copolymers of ethylene and one or more alpha-olefins having from 3 to 12 carbon atoms and a content of units derived from ethylene higher than 80% by mol can be obtained.

The following examples can further illustrate the present invention. Obviously, variations can be carried out without

10 departing from the scope of the present invention.

The properties indicated are determined according to the following methods:

- MIE flow index: ASTM D-1238
- MIF flow index: ASTM D-1238
- 15 - Flowability: the time employed by 100 g of polymer to flow through a funnel with a 1.5 cm diameter outlet hole and walls inclined at 20° to the vertical
- Bulk density: DIN-53194
- Morphology and granulometric distribution of the polymer particles: ASTM-D 1921-63
- Fraction soluble in xylene: determined at 25 °C
- 20 - Content of comonomer: percentage by weight of comonomer determined by I.R. spectrum
- Real density: ASTM 792-D
- Intrinsic viscosity: ASTM 2857-70

EXAMPLES

Preparation of the spherical support (Adduct $\text{MgCl}_2/\text{EtOH}$)

The magnesium chloride and alcohol adduct was prepared following the method described in Example 2 of USP 4,399,054, but working at 2000 rpm instead of 10,000 rpm. The adduct containing about 3 mol of alcohol had an 30 average size of about 60 μm with a dispersion range of about 30-90 μm .

General method for the preparation of the solid component

The spherical support prepared according to the above mentioned methods was subjected to thermal treatment 35 under N_2 stream, within the temperature range of 50-150 °C until spherical particles having a residual alcohol content of about 35% (1.1 mol of alcohol for each mol of MgCl_2) were obtained.

300 g of this support were introduced into a 5000 cm^3 reactor and suspended in 3000 cm^3 of anhydrous hexane. Whilst stirring and at room temperature, 130 g of AlEt_3 in hexane solution (107 g/l) were slowly introduced. The mixture was heated to 60 °C and kept at this temperature for 60 minutes. The stirring was stopped, and the mixture left to settle 40 and the clear phase was separated. The treatment was repeated twice more with AlEt_3 under the same conditions. Thereafter, the sediment was washed three times with anhydrous hexane and dried at 50 °C. The support thus obtained showed the following characteristics:

- residual OEt 5.5% (by weight)
- residual Al 3.6% (by weight)
- 45 - Mg 20.4% (by weight)

260 g of the support were introduced into a 5000 cm^3 reactor together with 3000 cm^3 of anhydrous hexane. The mixture was stirred and 242 g of Ti(OBu)_4 were fed at room temperature, over 30 minutes. The mixture was stirred for a further 30 minutes and thereafter 350 g of SiCl_4 diluted with 250 cm^3 of hexane were supplied over 30 minutes and at room temperature. The whole was heated to 65 °C over 40 minute and this temperature was kept for 3 hours, then separating the liquid phase by sedimentation and siphoning.

Thereafter, 7 washings with hexane (3000 cm^3 each time) were carried out, 3 of which of at 60 °C and 4 at room temperature. The component in spherical form was dried at 50 °C under vacuum.

55 The characteristics were as follows:

- Total Titanium 3.4% (by weight)
- Mg 17.1% (by weight)

- Si 0.9% (by weight)
- Cl 57.4% (by weight)
- Residual Al 1.3% (by weight)
- OEt 2.9% (by weight)
- 5 - OBu 13.2% (by weight)

EXAMPLE 1

Copolymerization of ethylene with 1-butene (LLDPE)

10 Into a 4 litre stainless steel autoclave, degassed under nitrogen stream for 2 hours at 70 °C and then washed with anhydrous propane, 0.01 g of solid component, 0.96 g of AlEt₃, 2-isopropyl-2-isoamyl-1,3-dimethoxypropane [electron donor compound (c)] mixed in 25 cm³ of hexane were introduced. The ratio by mol AlEt₃/electron donor compound was equal to 60. 800 g of anhydrous propane were finally introduced. The whole was heated to 75 °C and thereafter 15 2 bar of H₂ were introduced at the same time as 7 bar of ethylene and 350 g of 1-butene. During the polymerization the partial pressure of the ethylene was kept constant and 3 g of 1-butene were added for each 30 g of the ethylene supplied. After 3 hours the reaction was stopped by immediate purging of the reagent and propane. The results of the polymerization are reported in Table 1.

20 EXAMPLE 2 (COMPARISON)

The polymerization was carried out as described in Example 1, except that no electron donor component (c) was used. The results of the polymerization are reported in Table 1.

25 EXAMPLE 3

The same catalyst of Example 1 was used, with the difference that the electron donor compound (c) used was 2,2-diisobutyl-1,3-dimethoxypropane. The polymerization was carried out as in example 1 with the difference that instead of operating for 3 hours at 75 °C, it was carried out for 30 minutes at 30 °C and than for 2.5 hours at 75 °C. The 30 results are reported in Table 1.

EXAMPLE 4

35 The polymerization was carried out under the same conditions as example 3 with the only difference being that the electron donor compound (c) used was 2,2-diphenyl-1,3-dimethoxypropane. The results of the polymerization are reported in Table 1.

TABLE 1

Ex.	Yield Kg _{pol} /g _{cat}	MIE g\10'	F\ E	Bulk density (g/cm ³)	Density (g/cm ³)	Bonded butene (weight)	Insol in xylene (weight)
1	17.4	1	25.5	0.315	0.9213	8.4%	87.54%
2 com	22.5	1	30.0	0.31	0.9205	8.7%	82.61%
3	17.0	1	25.9	0.33	0.9259	3.6%	94.74%
4	13.8	1	24.2	0.335	0.925	4.6%	93.10%

50 Claims

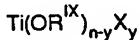
1. Catalysts for the polymerization of ethylene and mixtures thereof with olefines CH₂=CHR^{VIII}, where R^{VIII} is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms, comprising the reaction product of:
 - 55 (a) a solid catalyst component comprising a magnesium halide in the active form, as being characterized by X-ray spectrum wherein the most intense diffraction line appearing in the spectrum of the non active chloride is diminished in intensity and in said spectrum a halo appears with the maximum intensity shifted towards lower angles in comparison to that of the most intense line, and a titanium compound containing at least one

Ti-halogen bond;
 (b) an Al-alkyl compound;
 (c) an external electron donor compound selected from diethers,

5 said compound (c) being reactive towards $MgCl_2$ but not towards $AlEt_3$ under the standard reaction conditions.

2. Catalysts according to claim 1 wherein the electron donor compound (c) is a 1,3-diether.

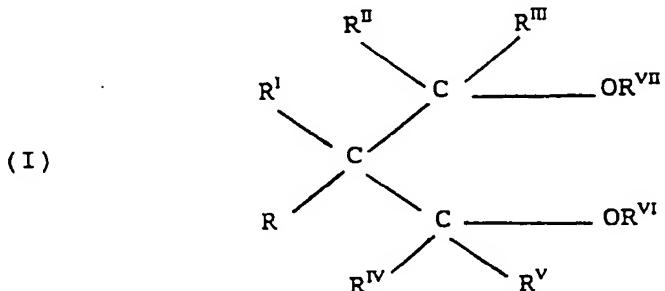
3. Catalysts according to claim 1, wherein the magnesium halide is a magnesium chloride and the titanium compound
 10 is selected from the compounds of formula:



15 wherein R^{IX} is a hydrocarbyl radical having 1-12 carbon atoms or a COR^{IX} group, X is halogen, n is the valence of titanium and y is a number comprised between 1 and n.

20 4. Catalysts according to claim 3, wherein the magnesium chloride is obtained by dealcholatation of $MgCl_2 \cdot PR^X OH$ adduct wherein P is a number from 1 to 6 and R^X is a hydrocarbyl radical having 1-12 carbon atoms.

5. Catalysts according to claim 1, wherein the electron donor compound (c) is selected from 1,3-diethers of the formula
 25 (I):



wherein R, R^I , R^{II} , R^{III} , R^{IV} , R^V , same or different from each other, are hydrogen or linear or branched alkyl radicals, cycloalkyl, aryl, alkyaryl or arylalkyl radicals having 1-18 carbon atoms, with the provision that R and R^I cannot both be hydrogen; R^{VI} and R^{VII} , same or different from each other, are linear or branched alkyl radicals, cycloalkyl, aryl, alkyaryl or arylalkyl radicals having 1-18 carbon atoms; when radicals from R^I to R^V are hydrogen and R^{VI} and R^{VII} are methyl, R cannot be methyl; at least two of said radicals from R to R^{VII} can be linked together to give one or more cyclic structures.

40 6. Catalysts according to claim 5 wherein R^{VI} and R^{VII} are methyl and R and R^I , same or different from each other, are selected from the group consisting of propyl, isopropyl, isobutyl, t-butyl, pentyl, isopentyl, cyclopentyl, hexyl, 1,5-dimethylhexyl, cyclohexyl, methylcyclohexyl, ethylcyclohexyl, heptyl, 3,7-dimethyloctyl, phenyl.

45 7. Catalysts according to claim 1, wherein the electron donor compound (c) is selected from the group consisting of 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-diphenyl-1,3-dimethoxypropane, 2,2-dibenzyl-1,3-dimethoxypropane, 2,2-bis-(cyclohexylmethyl)-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dibutoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2-isopentyl-2-isopropyl-1,3-dimethoxypropane, 2,2,4-trimethyl-1,3-dimethoxypentane, 1,1-bis(methoxymethyl)cyclohexane, (+/-)2,2-bis-(methoxymethyl)norbornane, 2-isopropyl-2-(3,7-dimethyloctyl)-1,3-dimethoxypropane, 2,2-diisopropyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropane, 2,2-diisopentyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, 2-heptyl-2-pentyl-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane, 2-isopropyl-2-isobutyl-1,3-dimethoxypropane.

8. Process for the polymerization of ethylene and mixtures thereof with olefines $\text{CH}_2=\text{CHR}^{\text{VIII}}$, where R^{VIII} is an alkyl, cycloalkyl or aryl radical having 1-12 carbon atoms, carried out in the presence of a catalyst comprising the reaction product of:

(a) a solid catalyst component comprising a magnesium halide in the active form, as being characterized by X-ray spectrum wherein the most intense diffraction line appearing in the spectrum of the non active chloride is diminished in intensity and in said spectrum a halo appears with the maximum intensity shifted towards lower angles in comparison to that of the most intense line, and a titanium compound containing at least one Ti-halogen bond;

(b) an Al-alkyl compound;

(c) an external electron donor compound selected from diethers,

said compound (c) being reactive with MgCl_2 , but not with Altriethyl under standard reaction conditions.

15. 9. Process according to claim 8 wherein the electron donor compound (c) is a 1,3-diether.

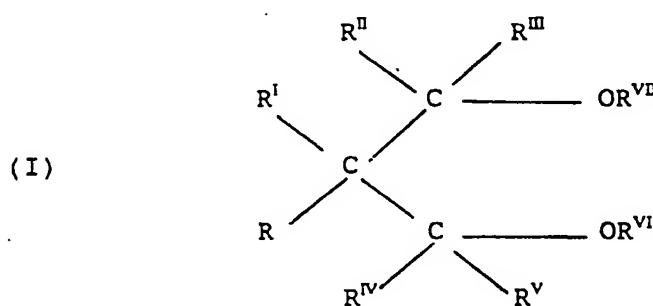
10. 10. Process according to claim 8 wherein the magnesium halide is magnesium chloride and the titanium compound is selected from the compounds of formula:



wherein R^{IX} is a hydrocarbyl radical having 1-12 carbon atoms or a COR^{IX} group, X is halogen, n is the valence of titanium and y is a number comprised between 1 and n.

25. 11. Process according to claim 10, wherein the magnesium chloride is obtained by dealcoholation of $\text{MgCl}_2\cdot\text{PR}^{\text{X}}\text{OH}$ adduct, wherein P is a number from 1 to 6 and R^{X} is a hydrocarbyl radical having 1-12 carbon atoms.

30. 12. Process according to claim 8 wherein the electron donor compound (c) is selected from 1,3-diethers of formula (I):



45. wherein R, R^1 , R^{II} , R^{IV} , R^{V} , same or different from each other, are hydrogen or linear or branched alkyl radicals, cycloalkyl, aryl, alkylaryl or arylalkyl radicals having 1-18 carbon atoms, with the provision that R and R^1 cannot both be hydrogen; R^{VI} and R^{VII} , same or different from each other, are linear or branched alkyl radicals, cycloalkyl, aryl, alkylaryl or arylalkyl radicals having 1-18 carbon atoms; when radicals from R^1 to R^{V} are hydrogen and R^{VI} and R^{VII} are methyl, R cannot be methyl; at least two of said radicals from R to R^{VI} can be linked together to give one or more cyclic structures.

50. 13. Process according to claim 12, wherein R^{VI} and R^{VII} are methyl and R and R^1 , same or different from each other are selected from the group consisting of propyl, isopropyl, isobutyl, t-butyl, pentyl, isopentyl, cyclopentyl, hexyl, 1,5-dimethylhexyl, cyclohexyl, methylcyclohexyl, ethylcyclohexyl, heptyl, 3,7-dimethyloctyl, phenyl.

55. 14. Process according to claim 8 wherein the electron donor compound (c) is selected from the group consisting of 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-diphenyl-1,3-dimethoxypropane, 2,2-dibenzyl-1,3-dimethoxypropane, 2,2-bis-(cyclohexylmethyl)-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dibutoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2-isopentyl-2-isopropyl-1,3-dimethoxypropane,

2,2,4-trimethyl-1,3-dimethoxypentane, 1,1-bis(methoxymethyl)cyclohexane, (+/-) 2,2-bis(methoxymethyl)norbornane, 2-isopropyl-2-(3,7-dimethyloctyl)-1,3-dimethoxypropane, 2,2-diisopropyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropane, 2,2-diisopentyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, 2-heptyl-2-pentyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane, 2-isopropyl-2-isobutyl-1,3-dimethoxypropane.

5 15. Process according to one or more of claims from 8 to 14 wherein the obtained polymer contains up to 20% by mol of one or more olefins $\text{CH}_2=\text{CHR}^{\text{VIII}}$.

10 16. Process according to claim 15 wherein the olefin $\text{CH}_2=\text{CHR}^{\text{VIII}}$ is selected from 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene.

15 **Patentansprüche**

1. Katalysatoren zur Polymerisation von Ethylen und Gemischen davon mit Olefinen $\text{CH}_2=\text{CHR}^{\text{VIII}}$, worin R^{VIII} einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-12 Kohlenstoffatomen darstellt, umfassend das Reaktionsprodukt von:

20 (a) einer festen Katalysatorkomponente, umfassend ein Magnesiumhalogenid in aktiver Form, gekennzeichnet durch ein Röntgenspektrum, worin die im Spektrum des nichtaktiven Chlorids erscheinende intensivste Beugungslinie in der Intensität verringert ist und in dem Spektrum eine Halo mit einer maximalen Intensität, verschoben zu den kleineren Winkeln im Vergleich zu jenem der intensivsten Linie, erscheint und eine Titanverbindung, enthaltend mindestens eine Ti-Halogenbindung;

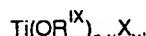
25 (b) eine Al-Alkylverbindung;

(c) eine äußere Elektronendonatorverbindung, ausgewählt aus Diethern,

30 wobei Verbindung (c) gegenüber MgCl_2 , jedoch nicht gegenüber AlEt_3 unter Standard-Reaktionsbedingungen reaktiv ist.

35 2. Katalysatoren nach Anspruch 1, wobei die Elektronendonatorverbindung (c) ein 1,3-Diether ist.

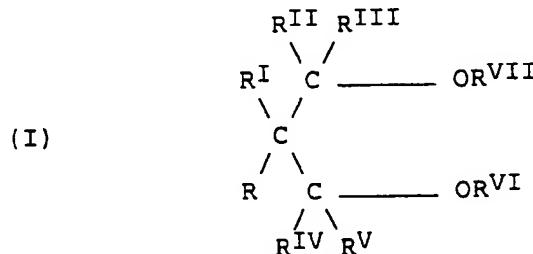
3. Katalysatoren nach Anspruch 1, wobei das Magnesiumhalogenid ein Magnesiumchlorid darstellt und die Titanverbindung ausgewählt ist aus den Verbindungen der Formel:



40 worin R^{IX} einen Kohlenwasserstoffrest mit 1-12 Kohlenstoffatomen oder eine Gruppe COR^{IX} darstellt, X Halogen darstellt, n die Wertigkeit von Titan ist und y eine Zahl, umfaßt zwischen 1 und n , ist.

45 4. Katalysatoren nach Anspruch 3, wobei das Magnesiumchlorid durch Entalkoholisierung des Addukts $\text{MgCl}_2 \cdot p\text{R}^{\text{X}}\text{OH}$, worin p eine Zahl von 1 bis 6 ist und R^{X} einen Kohlenwasserstoffrest mit 1-12 Kohlenstoffatomen darstellt, erhalten wird.

5. Katalysatoren nach Anspruch 1, wobei die Elektronendonatorverbindung (c) ausgewählt ist aus 1,3-Diethern der Formel (I):



worin R, R^I, R^{II}, R^{III}, R^{IV}, R^V, gleich oder verschieden voneinander, Wasserstoff oder lineare oder verzweigte Alkylreste, Cycloalkyl-, Aryl-, Alkylaryl- oder Arylalkylreste mit 1-18 Kohlenstoffatomen darstellen, mit der Maßgabe, daß R und R^I nicht beide Wasserstoff sein können; R^{VI} und R^{VII}, gleich oder verschieden voneinander, lineare oder verzweigte Alkylreste, Cycloalkyl-, Aryl-, Alkylaryloder Arylalkylreste mit 1-18 Kohlenstoffatomen darstellen; wenn die Reste von R^I bis R^V Wasserstoff sind und R^{VI} und R^{VII} Methyl sind, R nicht Methyl sein kann; wobei mindestens zwei der Reste R bis R^{VII} zu einer oder mehreren cyclischen Strukturen miteinander verbunden sein können.

5 6. Katalysatoren nach Anspruch 5, wobei R^{VI} und R^{VII} Methyl darstellen und R und R^I, gleich oder verschieden voneinander, ausgewählt sind aus der Gruppe, bestehend aus Propyl, Isopropyl, Isobutyl, t-Butyl, Pentyl, Isopentyl, Cyclopentyl, Hexyl, 1,5-Dimethylhexyl, Cyclohexyl, Methylcyclohexyl, Ethylcyclohexyl, Heptyl, 3,7-Dimethyloctyl, Phenyl.

10 7. Katalysatoren nach Anspruch 1, wobei die Elektronendonorverbindung (c) ausgewählt ist aus der Gruppe, bestehend aus 2-Methyl-2-isopropyl-1,3-dimethoxypropan, 2,2-Diisobutyl-1,3-dimethoxypropan, 2,2-Diphenyl-1,3-dimethoxypropan, 2,2-Dibenzyl-1,3-dimethoxypropan, 2,2-Bis-(cyclohexylmethyl)-1,3-dimethoxypropan, 2,2-Diisobutyl-1,3-dibutoxypropan, 2,2-Diisobutyl-1,3-dimethoxypropan, 2-Isopentyl-2-isopropyl-1,3-dimethoxypropan, 2,2,4-Trimethyl-1,3-dimethoxypentan, 1,1-Bis(methoxymethyl)cyclohexan, (+/-) 2,2-Bis(methoxymethyl)norbornan, 2-Isopropyl-2-(3,7-dimethyloctyl)-1,3-dimethoxypropan, 2,2-Diisopropyl-1,3-dimethoxypropan, 2-Isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropan, 2,2-Diisopentyl-1,3-dimethoxypropan, 2-Isopropyl-2-cyclohexyl-1,3-dimethoxypropan, 2-Isopropyl-2-cyclopentyl-1,3-dimethoxypropan, 2,2-Dicyclopentyl-1,3-dimethoxypropan, 2-Heptyl-2-pentyl-1,3-dimethoxypropan, 2,2-Dicyclohexyl-1,3-dimethoxypropan, 2,2-Dipropyl-1,3-dimethoxypropan, 2-Isopropyl-2-isobutyl-1,3-dimethoxypropan.

15 20 25 8. Verfahren zur Polymerisation von Ethylen und Gemischen davon mit Olefinen CH₂=CHR^{VIII}, worin R^{VIII} einen Alkyl-, Cycloalkyl- oder Arylrest mit 1-12 Kohlenstoffatomen darstellt, ausgeführt in Gegenwart eines Katalysators, umfassend das Reaktionsprodukt von:

30 (a) einer festen Katalysatorkomponente, umfassend ein Magnesiumhalogenid in aktiver Form, gekennzeichnet durch ein Röntgenspektrum, worin die im Spektrum des nichtaktiven Chlorids erscheinende intensivste Beugungslinie in der Intensität verringert ist und in dem Spektrum eine Halo mit einer maximalen Intensität, verschoben zu den kleineren Winkeln im Vergleich zu jenem der intensivsten Linie, erscheint und eine Titanverbindung, enthaltend mindestens eine Ti-Halogenbindung;

35 (b) eine Al-Alkylverbindung;

(c) eine äußere Elektronendonorverbindung, ausgewählt aus Diethern,

wobei Verbindung (c) mit MgCl₂, jedoch nicht mit AlTriethyl unter Standard-Reaktionsbedingungen reaktiv ist.

40 9. Verfahren nach Anspruch 8, wobei die Elektronendonorverbindung (c) ein 1,3-Diether ist.

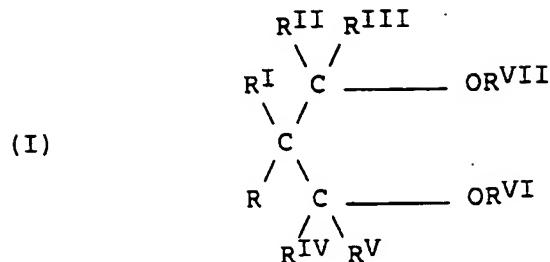
10. Verfahren nach Anspruch 8, wobei das Magnesiumhalogenid ein Magnesiumchlorid ist und die Titanverbindung ausgewählt ist aus den Verbindungen der Formel:

45 $Ti(OR^{IX})_{n-y}X_y$

worin R^{IX} einen Kohlenwasserstoffrest mit 1-12 Kohlenstoffatomen oder eine Gruppe COR^{IX} darstellt, X Halogen darstellt, n die Wertigkeit von Titan ist und y eine Zahl, umfaßt zwischen 1 und n, ist.

50 11. Verfahren nach Anspruch 10, wobei das Magnesiumchlorid durch Entalkoholisierung des Addukts MgCl₂·pRXOH, worin p eine Zahl von 1 bis 6 ist und RX einen Kohlenwasserstoffrest mit 1-12 Kohlenstoffatomen darstellt, erhalten wird.

12. Verfahren nach Anspruch 8, wobei die Elektronendonorverbindung (c) ausgewählt ist aus 1,3-Diethern der Formel (I):



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worin $\text{R}, \text{R}^{\text{I}}, \text{R}^{\text{II}}, \text{R}^{\text{III}}, \text{R}^{\text{IV}}, \text{R}^{\text{V}}$, gleich oder verschieden voneinander, Wasserstoff oder lineare oder verzweigte Alkylreste, Cycloalkyl-, Aryl-, Alkylaryl- oder Arylalkylreste mit 1-18 Kohlenstoffatomen darstellen, mit der Maßgabe, daß R und R^{I} nicht beide Wasserstoff sein können; R^{VI} und R^{VII} , gleich oder verschieden voneinander, lineare oder verzweigte Alkylreste, Cycloalkyl-, Aryl-, Alkylaryl- oder Arylalkylreste mit 1-18 Kohlenstoffatomen darstellen; wenn die Reste von R^{I} bis R^{V} Wasserstoff sind und R^{VI} und R^{VII} Methyl sind, R nicht Methyl sein kann; wobei mindestens zwei der Reste R bis R^{VII} zu einer oder mehreren cyclischen Strukturen miteinander verbunden sein können.

13. Verfahren nach Anspruch 12, wobei R^{VI} und R^{VII} Methyl darstellen und R und R^{I} , gleich oder verschieden voneinander, ausgewählt sind aus der Gruppe, bestehend aus Propyl, Isopropyl, Isobutyl, t-Butyl, Pentyl, Isopentyl, Cyclopentyl, Hexyl, 1,5-Dimethylhexyl, Cyclohexyl, Methylcyclohexyl, Ethylcyclohexyl, Heptyl, 3,7-Dimethyloctyl, Phenyl.

14. Verfahren nach Anspruch 8, wobei die Elektronendonorverbindung (c) ausgewählt ist aus der Gruppe, bestehend aus 2-Methyl-2-isopropyl-1,3-dimethoxypropan, 2,2-Diisobutyl-1,3-dimethoxypropan, 2,2-Diphenyl-1,3-dimethoxypropan, 2,2-Dibenzyl-1,3-dimethoxypropan, 2,2-Bis-(cyclohexylmethyl)-1,3-dimethoxypropan, 2,2-Diisobutyl-1,3-dibutoxypropan, 2,2-Disobutyl-1,3-dimethoxypropan, 2-Isopentyl-2-isopropyl-1,3-dimethoxypropan, 2,2,4-Trimethyl-1,3-dimethoxypentan, 1,1-Bis(methoxymethyl)cyclohexan, (+/-)2,2-Bis(methoxymethyl)norbornan, 2-Isopropyl-2-(3,7-dimethyloctyl)-1,3-dimethoxypropan, 2,2-Diisopropyl-1,3-dimethoxypropan, 2-Isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropan, 2,2-Diisopentyl-1,3-dimethoxypropan, 2-Isopropyl-2-cyclohexyl-1,3-dimethoxypropan, 2,2-Dicyclopentyl-1,3-dimethoxypropan, 2-Heptyl-2-pentyl-1,3-dimethoxypropan, 2-Isopropyl-2-cyclopentyl-1,3-dimethoxypropan, 2,2-Dicyclohexyl-1,3-dimethoxypropan, 2,2-Dipropyl-1,3-dimethoxypropan, 2-Isopropyl-2-isobutyl-1,3-dimethoxypropan.

15. Verfahren nach einem oder mehreren der Ansprüche 8 bis 14, wobei das erhaltene Polymer bis zu 20 Mol-% ein oder mehrere Olefine $\text{CH}_2=\text{CHR}^{\text{VIII}}$ enthält.

16. Verfahren nach Anspruch 15, wobei das Olefin $\text{CH}_2=\text{CHR}^{\text{VIII}}$ ausgewählt ist aus 1-Buten, 1-Penten, 4-Methyl-1-penten, 1-Hexen, 1-Octen.

Revendications

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1. Catalyseurs pour la polymérisation d'éthylène et de mélange d'éthylène avec des oléfines de formule $\text{CH}_2=\text{CHR}^{\text{VIII}}$, dans laquelle R^{VIII} est un radical alkyle, cycloalkyle ou aryle comportant 1 à 12 atomes de carbones comprenant le produit de la réaction de :

(a) un composant catalytique solide comprenant un halogénure de magnésium sous forme active caractérisé par un spectre de diffraction aux rayons X dans lequel la ligne de diffraction la plus intense apparaissant dans le spectre du chlorure inactif présente une intensité moindre et, dans ledit spectre, un halo apparaît dont l'intensité maximale est déplacée vers des angles inférieurs par rapport à celle de la ligne plus intense, et un dérivé de titane contenant au moins une liaison Ti-halogène ;

(b) un dérivé Al-alkyle ;

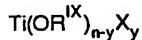
(c) un donneur d'électron externe sélectionné parmi les diéthers.

ledit composé (c) étant réactif envers MgCl_2 mais n'étant pas réactif envers AlEt_3 dans les conditions réactionnelles standard.

2. Catalyseurs selon la revendication 1, dans lesquels le donneur d'électron (c) est un 1,3-diéther.

3. Catalyseurs selon la revendication 1, dans lesquels l'halogénure de magnésium est du chlorure de magnésium et le dérivé de titane est sélectionné parmi les composés de formule

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dans laquelle :

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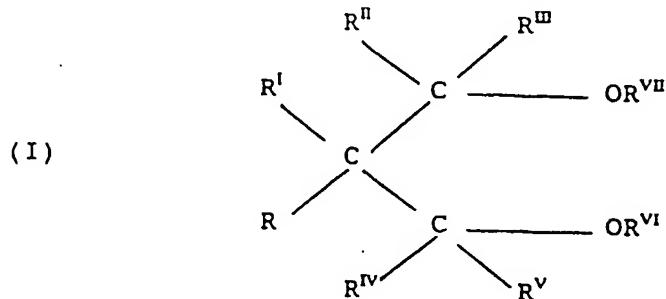
R^{IX} est un radical hydrocarbyle comportant 1 à 12 atomes de carbone ou un groupe COR^{IX} ;
 X est un halogène ;
 n représente la valence du titane ; et
 Y est un nombre compris entre 1 et n .

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4. Catalyseurs selon la revendication 3, dans lesquels le chlorure de magnésium est obtenu par déalcoolation du produit d'addition $\text{MgCl}_2\text{-PR}^{\text{X}}\text{OH}$, dans lequel P est un nombre compris entre 1 et 6 et R^{X} est un radical hydrocarbyle comportant 1 à 12 atomes de carbone.

20 5. Catalyseurs selon la revendication 1, dans lesquels le composé donneur d'électron (c) est sélectionné parmi les 1,3-diéthers de formule (I):

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dans laquelle R , R^1 , R^2 , R^3 , R^4 , R^5 , identiques ou différents les uns des autres, sont des radicaux hydrogène alkyles linéaires ou ramifiés, cycloalkyle, aryle, alkyl-aryle ou arylalkyle comportant 1 à 18 atomes de carbone, à la condition que R et R^1 ne représentent pas tous les deux un atome d'hydrogène ; R^6 et R^7 , identiques ou différents l'un de l'autre, sont des radicaux alkyles linéaires ou ramifiés, des radicaux cycloalkyle, aryle, alkylaryle ou arylalkyle comportant 1 à 18 atomes de carbone : lorsque les radicaux de R^1 à R^5 sont des atomes d'hydrogène et que R^6 et R^7 sont des radicaux méthyle, R ne peut pas être un radical méthyle; au moins deux desdits radicaux R à R^7 peuvent être liés pour former une ou plusieurs structures cycliques.

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6. Catalyseurs selon la revendication 5, dans lesquels R^6 et R^7 sont du méthyle, et R et R^1 , identiques ou différents l'un de l'autre, sont choisis parmi le groupe composé de propyle, isopropyle, isobutyle, t-butyle, pentyle, isopentyle, cyclopentyle, hexyle, 1,5-diméthylhexyle, cyclohexyle, méthylcyclohexyle, éthylcyclohexyle, heptyle, 3,7-diméthyloctyle, phényle.

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7. Catalyseurs selon la revendication 1, dans lesquels le composé donneur d'électron (c) est choisi dans le groupe composé de 2-méthyl-2-isopropyl-1,3-diméthoxypropane, 2,2-diisobutyl-1,3-diméthoxypropane, 2,2-diphényl-1,3-diméthoxypropane, 2,2-dibenzyl-1,3-diméthoxypropane, 2,2-bis-(cyclohexylméthyl)1,3-diméthoxypropane, 2,2-diisobutyl-1,3-dibutoxypropane, 2,2-diisobutyl-1,3-diméthoxypropane, 2-isopentyl-2-isopropyl-1,3-diméthoxypropane, 2,2,4-triméthyl-1,3-diméthoxypentane, 1,1-bis(méthoxyméthyl)-cyclohexane, (+/-)2,2-bis-(méthoxyméthyl)norbornane, 2-isopropyl-2-(3,7-diméthyloctyl)-1,3-diméthoxypropane, 2,2-diisopropyl-1,3-diméthoxypropane, 2-isopropyl-2-cyclohexylméthyl-1,3-diméthoxypropane, 2,2-diisopentyl-1,3-diméthoxypropane, 2-isopropyl-2-cyclohexyl-1,3-diméthoxypropane, 2-isopropyl-2-cyclopentyl-1,3-di-méthoxypropane, 2,2-dicyclopentyl-1,3-diméthoxypropane, 2-heptyl-2-pentyl-1,3-diméthoxypropane, 2,2-dicyclohexyl-1,3-diméthoxypropane, 2,2-dipropyl-méthoxypropane

1,3-diméthoxypropane, 2-isopropyl-2-isobutyl-1,3-diméthoxypropane.

5 8. Procédé de polymérisation d'éthylène et de mélanges d'éthylène avec des oléfines de formule $\text{CH}_2=\text{CHR}^{\text{VIII}}$, dans laquelle R^{VIII} est un radical alkyle, cycloalkyle ou aryle comportant 1 à 12 atomes de carbone, mis en œuvre en présence d'un catalyseur comprenant le produit de la réaction de :

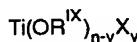
10 (a) un composant catalytique solide comprenant un halogénure de magnésium sous forme active caractérisé par un spectre de diffraction aux rayons X dans lequel la ligne de diffraction la plus intense apparaissant dans le spectre du chlorure inactif présente une intensité moindre et, dans ledit spectre, un halo apparaît dont l'intensité maximale est déplacée vers des angles inférieurs par rapport à celle de la ligne plus intense, et un dérivé de titane contenant au moins une liaison Ti-halogène ;

15 (b) un dérivé Al-alkyle ;
(c) un donneur d'électron externe sélectionné parmi les diéthers,

15 ledit composé (c) étant réactif envers MgCl_2 mais n'étant pas réactif envers AlEt_3 dans les conditions réactionnelles standard.

20 9. Procédé selon la revendication 8, dans lequel le composé donneur d'électron (c) est un 1,3-diéther.

20 10. Procédé selon la revendication 8, dans lequel l'halogénure de magnésium est du chlorure de magnésium et le dérivé de titane est sélectionné parmi les composés de formule :



dans laquelle :

RIX est un radical hydrocarbure comportant 1 à 12 atomes de carbone ou un groupe **CORIX** :

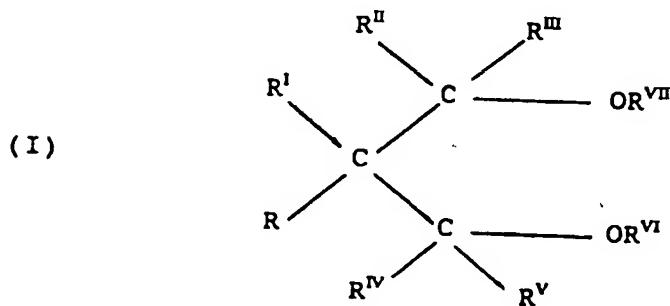
X est un halogène :

o représente la valence du titane : et

Y représente la valence du titan ; et Y est un nombre compris entre 1 et n.

35 11. Procédé selon la revendication 10, dans lequel le chlorure de magnésium est obtenu par déalcoolation du produit d'addition $MgCl_2 \cdot PR^XOH$, dans lequel P est un nombre compris entre 1 et 6 et R^X est un radical hydrocarbyle comportant 1 à 12 atomes de carbone.

12. Procédé selon la revendication 8, dans lequel le composeur donneur d'électron (c) est sélectionné parmi les 1,3-diéthers de formule (I) :



dans laquelle R, R^I, R^{II}, R^{III}, R^{IV}, R^V, identiques ou différents les uns des autres, sont des radicaux hydrogène alkyles linéaires ou ramifiés, cycloalkyle, aryle, alkylaryle ou arylalkyle comportant 1 à 18 atomes de carbone, à la condition que R et R^I ne représentent pas tous les deux un atome d'hydrogène ; R^{VI} et R^{VII}, identiques ou différents l'un de l'autre, sont des radicaux alkyles linéaires ou ramifiés, des radicaux cycloalkyle, aryle, alkylaryle ou arylalkyle comportant 1 à 18 atomes de carbone ; lorsque les radicaux de R^I à R^V sont des atomes d'hydrogène

et que R^{VI} et R^{VII} sont des radicaux méthyle, R ne peut pas être un radical méthyle ; au moins deux desdits radicaux R à R^{VII} peuvent être liés pour former une ou plusieurs structures cycliques.

5 13. Procédé selon la revendication 12, dans lequel R^{VI} et R^{VII} sont du méthyle, et R et R^I, identiques ou différents l'un de l'autre, sont choisis dans le groupe composé de propyle, isopropyle, isobutyle, t-butyle, pentyle, isopentyle, cyclopentyle, hexyle, 1,5-diméthylhexyle, cyclohexyle, méthylcyclohexyle, éthylcyclohexyle, heptyle, 3,7-diméthyloctyle, phényle.

10 14. Procédé selon la revendication 8, dans lequel le donneur d'électron (c) est choisi dans le groupe composé de 2-méthyl-2-isopropyl-1,3-diméthoxypropane, 2,2-diisobutyl-1,3-diméthoxypropane, 2,2-diphényl-1,3-diméthoxypropane, 2,2-dibenzyl-1,3-diméthoxypropane, 2,2-bis-(cyclohexylméthyl)-1,3-diméthoxypropane, 2,2-diisobutyl-1,3-dibutoxypropane, 2,2-diisobutyl-1,3-diméthoxypropane, 2-isopentyl-2-isopropyl-1,3-diméthoxypropane, 2,2,4-triméthyl-1,3-diméthoxypentane, 1,1-bis(méthoxyméthyl)-cyclohexane, (+/-)2,2-bis-(méthoxyméthyl)norbornane, 2-isopropyl-2-(3,7-diméthyloctyl)-1,3-diméthoxypropane, 2,2-diisopropyl-1,3-diméthoxypropane, 2-isopropyl-2-cyclohexylméthyl-1,3-diméthoxypropane, 2,2-diisopentyl-1,3-diméthoxypropane, 2-isopropyl-2-cyclohexyl-1,3-diméthoxypropane, 2-isopropyl-2-cyclopentyl-1,3-diméthoxypropane, 2,2-dicyclopentyl-1,3-diméthoxypropane, 2-heptyl-2-pentyl-1,3-diméthoxypropane, 2,2-dicyclohexyl-1,3-diméthoxypropane, 2,2-dipropyl-1,3-diméthoxypropane, 2-isopropyl-2-isobutyl-1,3-diméthoxypropane.

15 20 15. Procédé selon une ou plusieurs des revendications 8 à 14, dans lequel le polymère obtenu contient jusqu'à 20 % en moles d'une ou plusieurs oléfines de formule $\text{CH}_2=\text{CHR}^{\text{VIII}}$.

20 16. Procédé selon la revendication 15, dans lequel l'oléfine de formule $\text{CH}_2=\text{CHR}^{\text{VIII}}$ est sélectionnée parmi 1-butène, 1-pentène, 4-méthyl-1-pentène, 1-hexène et 1-octène.

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